

Photoacoustic Detection of Particulate Carbon

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PHOTOACOUSTIC DETECTION OF
PARTICULATE CARBON

by

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TECHNICAL REVIEW

This research report was accepted as a master's thesis and thus has been technically reviewed by academic peers.

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ABSTRACT

A photoacoustic technique for the mass monitoring of carbonaceous aerosols deposited on filter substrates has been developed. The technique involves the use of a specially designed photoacoustic cell. Photoacoustic response is calibrated as a function of elemental carbon loading using laboratory-generated elemental carbon standards. The nature of the photoacoustic response is examined at several chopping frequencies using these calibration standards, and the physical principles necessary for an adequate interpretation of the experimental results is presented in detail. Practical considerations concerning ambient carbon monitoring are outlined; in particular, the perturbation due to the presence of scattering particulates is examined and limited experimental quantification of this perturbation is reported.

INTRODUCTION

One widely used technique for the study of suspended particulate matter in the atmosphere consists of passing known volumes of air through various filter materials. The material deposited on the filters may then be taken to the laboratory, where a variety of techniques can be utilized in an attempt to quantitatively determine the relative amounts of specific chemical species on the filter. The ultimate goal in this type of process is to achieve a detailed mass balance, where all chemical species present on the filter are accounted for in correct proportion. Investigators are presently able to account for about 60-70%⁽¹⁾ of the total mass deposited on these filters, and this percentage is increasing steadily with time.

A simple visual examination of a piece of white filter material which has been "field loaded" will reveal that, in almost all cases, the collected material has a greyish appearance, indicating that the absorbing component of atmospheric particulate exhibits more or less uniform absorption across the visible spectrum. This might lead one to expect that the major absorbing component of atmospheric particulates is soot since it is both ubiquitous and grey. To demonstrate that this is indeed the case, Rosen et al.⁽²⁾ performed a set of Raman scattering experiments in which they determined that the major absorbing species in atmospheric particulates is polycrystalline graphite; hence referred to as graphitic, elemental, or inorganic carbon. Therefore, in what follows, we shall distinguish between this elemental carbon and carbon compounds which we shall refer to as the "organic" carbon component of the collected sample.

A precise knowledge of the absorbing component relative to the non-absorbing, scattering component of atmospheric particulate is important for several reasons. Both types of particles will have an effect on the climate⁽⁴⁻⁷⁾ since absorbing particles would tend to increase the global temperature and scattering particles would tend to decrease the global temperature by increasing the global albedo. Also, the same two effects lead to visibility degradation. The question of what adverse health effects would accompany an abundance of any foreign matter in the atmosphere is an important consideration. One group of investigators⁽⁸⁾ have also concluded that elemental carbon can act as a catalyst in chemical processes in the atmosphere. Soot is primarily produced by combustion processes. As our oil supplies diminish and increased demand is placed on less "clean" combustion sources it will become more and more important to obtain accurate information on ambient soot concentrations so that proper control strategies can be implemented.

Several methods exist for the determination of ambient elemental and organic carbon. Total, or elemental plus organic carbon, can be analyzed by proton inelastic scattering⁽⁹⁾ and by proton elastic scattering⁽¹⁰⁾. A well established combustion analysis^(9, 11-14) can reveal both the organic and elemental component by heating the sample in inert and oxydizing atmospheres separately. Since it appears that elemental carbon is primarily responsible for absorption, a variety of absorptive methods have been developed to measure elemental carbon. A few groups^(2, 14-17) have studied the degree to which light is passed through field loaded filters to infer an elemental carbon loading. Others⁽¹⁸⁻²⁰⁾ have studied the light reflected from the filter surface. The photoacoustic signal arising from suspended carbon particles in an

acoustically resonant cell has been used⁽²¹⁻²³⁾ to build a sensitive real-time carbon monitor. Although one group⁽²⁴⁾ has studied the photoacoustic signal arising from carbon particles deposited on filter substrates to infer information regarding elemental carbon, their system was not calibrated for use as an ambient carbon monitor. Hence, in what follows, we report on the generation of carefully prepared elemental carbon standards and the use of these standards to characterize the photoacoustic response to elemental carbon on field loaded filters. We have also used these calibration filters to compare the photoacoustic and optical transmission methods.

The importance of the calibration procedure cannot be overstated; ambient aerosols contain scattering as well as absorbing particles. Hence, it is important to first understand how these detection systems respond in the absence of scattering particles so that the perturbation associated with the scattering components can be considered separately. Hopefully, the perturbation may be quantified in order that accurate ambient carbon levels may be deduced.

The photoacoustic effect in solids is a fascinating subject in its own right. As will become evident later, the very thin carbon samples prepared in this study offer an excellent basis from which to study the photoacoustic effect. However, this means that a firm understanding of the physics involved in the photoacoustic process is essential for an adequate understanding of the experimental results. We shall, therefore, spend a good deal of time discussing the necessary physical principles and relating them to the mechanisms underlying the production of the photoacoustic signal.

In Section I we will review the theory of the photoacoustic effect in solids that is appropriate for our considerations. After establishing the familiar form of the photoacoustic response, we will use a different method to arrive at the same formula cast in a different algebraic form that better illustrates the physical processes involved in the production of the acoustic signal. In Section II we will give an analysis of the optical transmission method. Section III describes the experimental details of the study and Section IV gives the experimental results. Section V deals with the practical considerations relating to the use of both photoacoustic detection and optical attenuation as means of establishing ambient soot concentrations.

I. THE PHOTOACOUSTIC EFFECT IN SOLIDS

The photoacoustic effect, first reported in 1881 by Tyndall⁽²⁵⁾, Rontgen⁽²⁶⁾ and Bell⁽²⁷⁾, has become an important analytical tool for the investigation of gases, liquids, and solids. Several authors⁽²⁸⁻³³⁾ have presented theoretical treatments of the photoacoustic effect in solids, and, in most cases, have calculated the acoustic signal arising from two sources: 1) the heat flow from the sample to the surrounding gas and the corresponding acoustic signal resulting from the response of the gas to this heat fluctuation, and 2) the acoustic signal arising directly from the expansion and contraction of the sample as it heats and cools. The expression for the photoacoustic signal which takes into account both of these processes is algebraically forbidding and is usually analyzed on a computer. However, we are fortunate in that the samples used for this study are very highly absorbing (absorption coefficient $>10^5 \text{ cm}^{-1}$) and hence very thin. Therefore we expect process 2 above to contribute negligibly to our response and hence use the theory of Rosencwaig and Gersho⁽³¹⁾ to account for the photoacoustic signal due to elemental carbon. This greatly simplifies our problem and results in relatively simple algebraic manipulations.

Before entering into a detailed analysis of the photoacoustic effect we show a schematic in Fig. 1 of the detection cell and present an overview of the physical processes involved in the production of the acoustic signal within the cell. The sample is deposited on a non-absorbing, and for the moment, non-reflecting backing. The cell is filled with a non-absorbing gas and is equipped with non-absorbing input and output windows. Monochromatic light of intensity I_0 is amplitude modulated

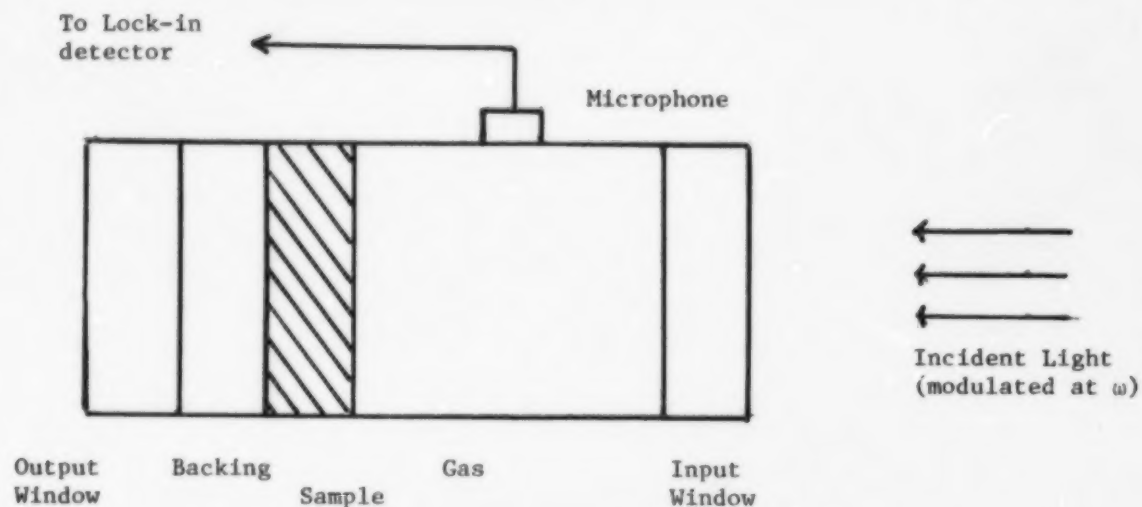


Fig. 1. Schematic of a photoacoustic cell

at frequency $\omega/2\pi$ before impinging upon the sample. A portion of this light is absorbed by the sample, and the absorbed light is converted into heat with a conversion efficiency which we shall assume to be unity. Assuming that the chopped radiation is perfectly sinusoidal, the resulting thermal disturbance within the sample will consist of two parts; a periodic temperature fluctuation at angular frequency ω and a nonperiodic temperature rise. The periodic temperature disturbance will propagate to the sample-gas boundary and heat a boundary layer of gas adjacent to the sample. The gas will respond to the periodic temperature fluctuations by expanding and contracting, acting as a piston to produce a periodic acoustic signal which is detected by a microphone. The output of the microphone then passes to a lock-in amplifier adjusted to detect only signals at angular frequency ω . The nonperiodic

temperature rise of the gas is a negligible effect for cells with metallic walls. We seek, then, to relate this steady state periodic acoustic signal at angular frequency ω to the thermal and absorptive properties of the sample.

In order to understand just how these periodic thermal disturbances propagate we consider briefly the thermal diffusion equation. In one dimension, we have

$$\rho C \frac{\partial \phi(x, t)}{\partial t} - k \frac{\partial^2 \phi(x, t)}{\partial x^2} = f(x, t) \quad (1)$$

where

$\phi(x, t)$ is the temperature at point x for time t ,

C is the specific heat in $\frac{\text{Joules}}{\text{g } ^\circ\text{K}}$,

ρ is the density in g/cm^3 ,

k is the thermal conductivity in $\frac{\text{Watts}}{\text{cm } ^\circ\text{K}}$,

$f(x, t)$ is the volume heat source density at point x and time t in $\frac{\text{Watts}}{\text{cm}^3}$.

It is assumed that the thermal conductivity k is constant throughout the region of interest.

Dividing Eq. 1 by k and rearranging, we have

$$\frac{\partial^2 \phi}{\partial x^2} - \frac{1}{\alpha} \frac{\partial \phi}{\partial t} = \frac{f}{k} \quad \text{where}$$

$\alpha = \frac{k}{\rho C}$ is the thermal diffusivity in cm^2/sec .

Consider, for the moment, the homogeneous equation:

$$\frac{\partial^2 \phi}{\partial x^2} - \frac{1}{\alpha} \frac{\partial \phi}{\partial t} = 0.$$

As stated above, our detection system is sensitive only to periodic temperature (or pressure) fluctuations at the particular frequencies $\omega/2\pi$. Hence, we let

$$\phi(x, t) = \phi(x) e^{j\omega t}$$

where $j = \sqrt{-1}$. This gives

$$\frac{\partial^2 \phi(x)}{\partial x^2} - \sigma^2 \phi(x) = 0, \quad (2)$$

where $\sigma^2 = \frac{j\omega}{\alpha}$ and $\sigma = (1 + j) \sqrt{\frac{\omega}{2\alpha}}$

Therefore, we see that the solution to equation 2 is

$$\phi(x) = B e^{+\sigma x} + F e^{-\sigma x}$$

or

$$\phi(x, t) = B e^{j\omega t + \sigma x} + F e^{j\omega t - \sigma x}$$

The first term on the R. H. S. represents a traveling thermal wave propagating in the $-x$ direction and the second term a traveling thermal wave propagating in the $+x$ direction. If $a = \sqrt{\frac{\omega}{2\alpha}}$ in cm^{-1} , the forward traveling wave can be written as

$$\phi_+(x, t) = F e^{-ax} e^{j(\omega t - ax)}$$

Thus, we see that this is a rapidly damped thermal wave with wavenumber a and wavelength $2\pi/a$. In what follows, we shall repeatedly use the fact that this wave is very rapidly damped; in one thermal wavelength the wave will be diminished by a factor of $e^{-2\pi}$. Note that the thermal wavelength depends inversely upon the square root of the chopping frequency.

We are now in a position to solve for the steady state periodic pressure fluctuations within the cell. To do this, we consider only the periodic temperature fluctuations within the sample, backing, and gas portions of the cell as shown in Fig. 2. The backing and gas layers

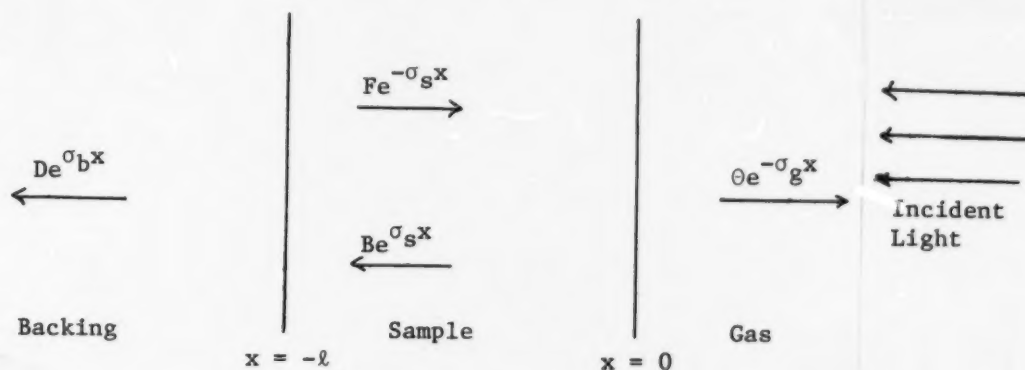


Fig. 2. Steady state thermal waves within the cell

are assumed to be thicker than one thermal wavelength in that medium, so that there is only a backward traveling wave in the backing and a forward traveling wave in the gas.

If the incident light flux in $\frac{\text{Watts}}{\text{cm}^2}$ is represented by

$$I = \frac{I_0}{2} (1 + \cos \omega t),$$

then the energy absorbed per second per cm^3 by the sample is then given by

$$\begin{aligned} H &= \frac{\beta I_0}{2} e^{\beta x} (1 + \cos \omega t) \\ &= \frac{\beta I_0}{2} e^{\beta x} + \frac{\beta I_0}{2} e^{\beta x} \cos \omega t \end{aligned} \quad (3)$$

with x taking negative values within the sample. The first term on the R. H. S. contributes to a steady non-periodic temperature rise and will be neglected as discussed above. Therefore, we let the volume heat source density in the sample be

$$f(x, t) = \frac{\beta I_0}{2} e^{\beta x} e^{j\omega t} \quad -l < x < 0.$$

We seek to solve for the amplitude θ of the thermal wave in the gas region of the cell (see Fig. 2) since it is this wave that produces the acoustic signal. In solving the thermal diffusion equation in each region, we again let $\phi(x, t) = \phi(x) e^{j\omega t}$ and henceforth drop the tilde on $\phi(x)$. Thus, in the backing region, we have

$$\frac{\partial^2 \phi_b}{\partial x^2} - \sigma_b^2 \phi_b = 0, \quad x < -l \quad (4)$$

with $\phi_b = De^{-\sigma_b x}$

In the sample region, we have

$$\frac{\partial^2 \phi_s}{\partial x^2} - \sigma_s^2 \phi_s = Ae^{\beta x} \quad -l < x < 0 \quad (5)$$

with $A = \frac{\beta I_0}{2k_s}$

The homogeneous solution to equation 5 is $Fe^{-\sigma_s x} + Be^{\sigma_s x}$, and the particular solution is $Ee^{\beta x}$. Substituting $\phi_s = Fe^{-\sigma_s x} + Be^{\sigma_s x} + Ee^{\beta x}$ into Eq. 5 gives

$$E = \frac{A}{\beta^2 - \sigma_s^2} = -\frac{\beta I_0}{2k_s(\beta^2 - \sigma_s^2)} \quad (6)$$

In the gas region, we have

$$\frac{\partial^2 \phi_g}{\partial x^2} - \sigma_g^2 \phi_g = 0, \quad x > 0$$

with $\phi_g = \theta e^{-\sigma_g x}$.

In summary, the amplitudes of the steady state periodic temperature fluctuations in each of the three regions are:

backing: $\phi_b = De^{\sigma_b x}$

sample: $\phi_s = Fe^{-\sigma_s x} + Be^{\sigma_s x} + Ee^{\beta x}$

gas: $\phi_g = \theta e^{-\sigma_g x}$

These solutions are subject to the boundary conditions of temperature continuity:

$$\phi_b(-l) = \phi_s(-l) \quad (7)$$

$$\phi_s(0) = \phi_g(0) \quad (8)$$

and flux continuity:

$$k_b \frac{\partial \phi_b}{\partial x}(-l) = k_s \frac{\partial \phi_s}{\partial x}(-l) \quad (9)$$

$$k_s \frac{\partial \phi_s}{\partial x}(0) = k_g \frac{\partial \phi_g}{\partial x}(0) \quad (10)$$

at the boundaries.

Hence,

Eq. (7) implies

$$\theta = F + B + E,$$

Eq. (9) implies

$$-k_g \sigma_g \theta = k_s (-\sigma_s F + \sigma_s B + \beta E),$$

Eq. (8) implies

$$De^{-\sigma_b l} = Fe^{\sigma_s l} + Be^{-\sigma_s l} + Ee^{-\beta l},$$

Eq. (10) implies

$$k_b \sigma_b De^{-\sigma_b l} = k_s (-\sigma_s F e^{\sigma_s l} + \sigma_s B e^{-\sigma_s l} + \beta E e^{-\beta l}).$$

If we define

$$b = \frac{k_b \sigma_b}{k_s \sigma_s}$$

$$g = \frac{k_g \sigma_g}{k_s \sigma_s}$$

$$r = \frac{\beta}{\sigma_s}$$

we may write the above four equations in matrix form:

$$\begin{pmatrix} 1 & 1 & -1 & 0 \\ 1 & -1 & -g & 0 \\ e^{\sigma s^l} & e^{-\sigma s^l} & 0 & -e^{-\sigma b^l} \\ e^{\sigma s^l} & -e^{-\sigma s^l} & 0 & be^{-\sigma b^l} \end{pmatrix} \begin{pmatrix} F \\ B \\ \theta \\ D \end{pmatrix} = \begin{pmatrix} -E \\ rE \\ -Ee^{-\beta l} \\ rEe^{-\beta l} \end{pmatrix}$$

We shall use Cramer's rule (34) to obtain the explicit form of the coefficient θ . To do this, we must evaluate the following determinants:

$$\begin{vmatrix} 1 & 1 & -1 & 0 \\ 1 & -1 & -g & 0 \\ e^{\sigma s^l} & e^{-\sigma s^l} & 0 & -e^{-\sigma b^l} \\ e^{\sigma s^l} & -e^{-\sigma s^l} & 0 & be^{-\sigma b^l} \end{vmatrix}$$

$$= be^{-\sigma b^l} \begin{vmatrix} 1 & 1 & -1 \\ 1 & -1 & -g \\ e^{\sigma s^l} & e^{-\sigma s^l} & 0 \end{vmatrix} + e^{-\sigma b^l} \begin{vmatrix} 1 & 1 & -1 \\ 1 & -1 & -g \\ e^{\sigma s^l} & -e^{-\sigma s^l} & 0 \end{vmatrix}$$

$$= -e^{-\sigma b^l} [e^{\sigma s^l} (1+g)(1+b) - e^{-\sigma s^l} (1-g)(1-b)] \quad (11)$$

Also

$$\begin{vmatrix} 1 & 1 & -E & 0 \\ 1 & -1 & rE & 0 \\ e^{\sigma s^l} & e^{-\sigma s^l} & -Ee^{-\beta l} & -e^{-\sigma b^l} \\ e^{\sigma s^l} & -e^{-\sigma s^l} & rEe^{-\beta l} & be^{-\sigma b^l} \end{vmatrix}$$

$$= be^{-\sigma b^l} \begin{vmatrix} 1 & 1 & -E \\ 1 & -1 & rE \\ e^{\sigma s^l} & e^{-\sigma s^l} & -Ee^{-\beta l} \end{vmatrix} + e^{-\sigma b^l} \begin{vmatrix} 1 & 1 & -E \\ 1 & -1 & rE \\ e^{\sigma s^l} & -e^{-\sigma s^l} & rEe^{-\beta l} \end{vmatrix}$$

$$= e^{-\sigma b^l} E [e^{\sigma s^l} (r-1)(b+1) - e^{-\sigma s^l} (r+1)(b-1) + 2(b-r) e^{-\beta l}] \quad (12)$$

By Cramer's rule, the coefficient θ is obtained by dividing Eq. (12) by Eq. (11). This gives

$$\theta = \frac{\beta I_0}{2k_s(\beta^2 - \sigma_s^2)} \left\{ \frac{[(r-1)(b+1)e^{\sigma_s l} - (r+1)(b-1)e^{-\sigma_s l} + 2(b-r)e^{-\beta l}]}{[(g+1)(b+1)e^{\sigma_s l} - (g-1)(b-1)e^{-\sigma_s l}]} \right\} \quad (13)$$

This is the amplitude of the transmitted thermal wave in the gas region as derived by Rosencwaig and Gersho.

The thermal wave in this region has the form

$$\phi_g(x, t) = \theta e^{-a_g x} e^{j(\omega t - a_g x)}$$

As mentioned above, this wave is rapidly damped. Therefore, we define a boundary layer of gas immediately adjacent to the sample of thickness $\lambda_g = \pi/a_g$. It is this boundary layer of gas that responds to the thermal waves transmitted from the sample, acting as a piston to produce the periodic pressure signal which is detected by the microphone.

To estimate the amplitude of this acoustic signal, we first spatially average the temperature fluctuation over the boundary layer:

$$\bar{\phi}(t) = \frac{1}{\lambda_g} \int_0^{\lambda_g} \theta e^{j(\omega t - \sigma_g x)} dx = \frac{1}{\pi/2} \theta e^{j(\omega t - \pi/4)}$$

To estimate the displacement of the gas piston, we use the ideal gas law:

$$\frac{V_0 + \delta V(t)}{T_0 + \bar{\phi}(t)} = \frac{V_0}{T_0}$$

or

$$\delta V(t) = \frac{V_0 \bar{\phi}(t)}{T_0}.$$

In our one dimensional case

$$V_0 = \lambda_g$$

$$\delta V(t) = \delta x(t)$$

so that

$$\begin{aligned}\delta x(t) &= \frac{\lambda_g \bar{\phi}(t)}{T_0} \\ &= \frac{\theta e^{j(\omega t - \pi/4)}}{\sqrt{2} a_g T_0}.\end{aligned}$$

Assuming that the rest of the gas responds adiabatically to this boundary piston, we have

$$PV^\gamma = \text{const}$$

Where V is the volume of the cell and P is the pressure in the cell. Hence,

$$\ln(P) + \gamma \ln(V) = \ln(\text{const})$$

or

$$\frac{\delta P}{P} + \gamma \frac{\delta V}{V} = 0$$

Noting that $\delta V = -\delta x(t)$, we have

$$\delta P(t) = \frac{\gamma P \delta x(t)}{\lambda_g}$$

where we have let the length of the gas portion of the cell $\lambda_g = V$. We see then that the pressure fluctuation within the cell is given by

$$\begin{aligned}\delta P(t) &= \frac{\delta P \theta e^{j(\omega t - \pi/4)}}{\sqrt{2} \lambda_g a_g T_0} \\ &= \frac{\gamma P |\theta|}{\sqrt{2} \lambda_g a_g T_0} e^{j(\omega t - \pi/4 + \phi)}\end{aligned}$$

$$\text{where } \tan^{-1} \phi = \frac{\text{Im} \theta}{\text{Re} \theta}$$

and where θ is defined above. The actual pressure variation detected by the microphone is then

$$\Delta P(t) = \text{Re} \delta P(t) = \frac{\gamma P |\theta|}{\sqrt{2} \lambda_g a_g T_0} \cos(\omega t - \pi/4 + \phi)$$

Note that the acoustic signal is inversely proportional to the temperature in the cell. Again we point out that the steady nonperiodic temperature rise ignored above is eliminated by metallic cell walls.

We have, up to this point, formally solved the boundary value problem appropriate to our considerations without attempting to physically interpret the rather complicated expression that we obtained. We shall now attack the problem from a slightly different viewpoint in an attempt to cast the solution in a more physical form.

Consider Fig. 3 where a thermal wave is incident on a boundary. Region 1

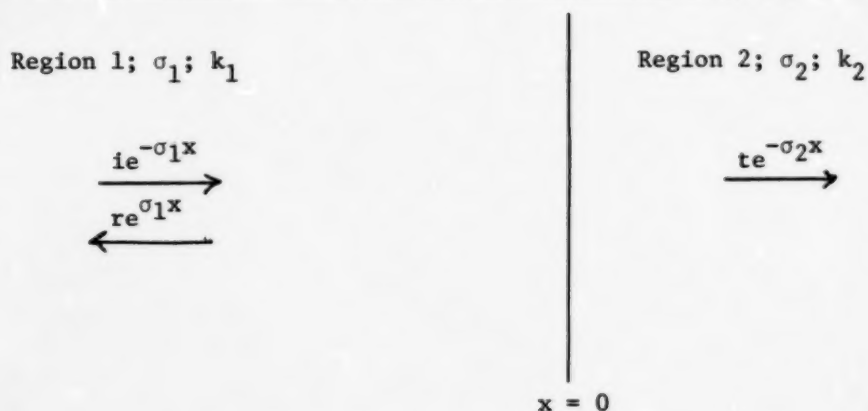


Fig. 3 Thermal wave incident in Region 1 on a boundary at $x = 0$ with the reflected and transmitted waves shown.

has thermal parameters σ_1 and k_1 , and region 2 has thermal parameters k_2 and σ_2 . The incident wave has amplitude i , the reflected wave has amplitude r , and the transmitted wave has amplitude t . The boundary is located at $x = 0$. Applying the conditions of temperature and flux continuity at the boundary leads to:

$$i + r = t \quad (14)$$

and

$$i - r = \alpha t \quad (15)$$

where

$$\alpha = \frac{k_2 \sigma_2}{k_1 \sigma_1}$$

$$= \sqrt{\frac{k_2^p c_2}{k_1^p c_1}} .$$

The thermal wave reflection coefficient R is defined to be ()

$$R \equiv \frac{|\text{amplitude of reflected wave}|}{|\text{amplitude of incident wave}|}$$

$$= \left| \frac{r}{i} \right|$$

By Eqs. (14) and (15) above,

$$R = \frac{1 - \alpha}{1 + \alpha} . \quad (16)$$

Similarly, the thermal wave transmission coefficient T is defined to be ()

$$T = \frac{|\text{amplitude of transmitted wave}|}{|\text{amplitude of incident wave}|}$$

or

$$T = \frac{2}{1 + \alpha} . \quad (17)$$

It is worth noting that a similar analysis using the corresponding heat flux waves leads to transmission and reflection coefficients which are consistent with the conservation of energy. It makes no difference which set of waves are used for the following analysis; we shall use thermal waves in order to be consistent with the preceding calculations.

The amplitude of the thermal wave transmitted to the gas will now be computed by considering multiple reflections of thermal waves between the sample-backing and the sample gas boundaries.

Consider Fig. 4 below ; again we let the incident light intensity

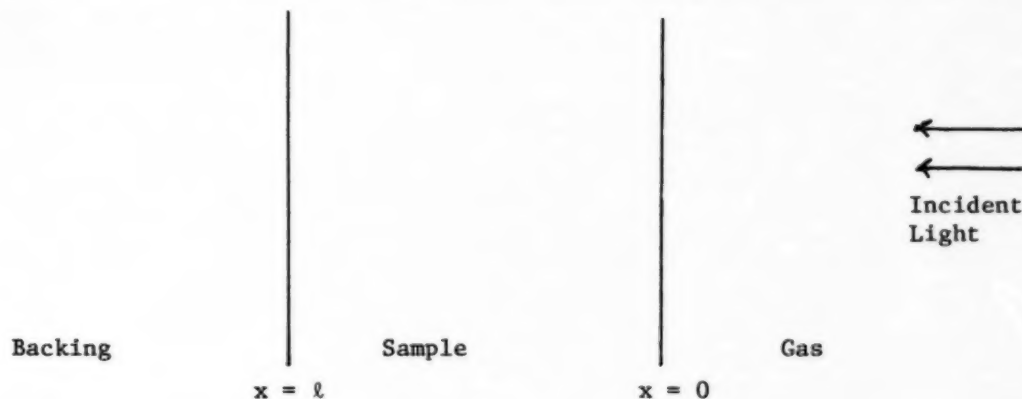


Fig. 4 Sample-backing and sample-gas boundaries.

be $\frac{1}{2}I_0(1 + \cos\omega t)$ and ignore the nonperiodic term. In steady state, the heat flux generated by light absorbed between x and $x + dx$ is

$$\frac{I_0\beta}{2} e^{-\beta x} dx.$$

The corresponding thermal waves have initial amplitude at x equal to

$$\frac{I_0\beta e^{-\beta x} dx}{4k_s\sigma_s}$$

In our one-dimensional case, the absorbed light at x initiates a thermal wave which travels towards the backing and one which travels towards the gas. Consider first the thermal wave initially traveling towards the gas. When it reaches the $x = 0$ boundary, part is reflected and part is transmitted to the gas. The reflected part travels to the $x = 0$ boundary, is reflected, and then travels to the $x = 0$ boundary where part of the remaining wave is again transmitted to the gas. In general, there will be an infinite number of these multiple reflections, and a corresponding infinite series of transmitted terms. If we add all of these terms

together, keeping track of the total distance that each term has traveled through the sample, we obtain

$$\begin{aligned} & \frac{I_0 \beta \exp(-\beta x) dx}{4k_s \sigma_s} [T_g \exp(-\sigma_s x) + R_b R_g T_g \exp[-(2\ell + x)\sigma_s] + \dots \\ & + (R_b R_g)^n T_g \exp[-(2n\ell + x)\sigma_s] + \dots] \\ & = I_0 \beta \exp[-(\beta + \sigma_s x)] dx / 4k_s \sigma_s [1 - R_b R_g \exp(-2\sigma_s \ell)] \end{aligned}$$

where, by Eqs. (16), (17)

$$T_g = \frac{2}{1 + g}$$

$$R_g = \frac{1 - g}{1 + g}$$

$$R_b = \frac{1 - b}{1 + b}$$

Similarly, the wave that initially travels towards the backing contributes a transmitted thermal wave at zero with amplitude

$$\begin{aligned} & \frac{I_0 \beta \exp(-\beta x) dx}{k_s \sigma_s} [R_g T_g \exp-(2\ell - x)\sigma_s] \\ & + R_b R_g R_b T_g \exp[-(4\ell - x)\sigma_s] + \dots \\ & + R_b T_g (R_b R_g)^n \exp[-(2(n + 1) - x)\sigma_s] + \dots \\ & = I_0 \beta \exp(-2\sigma_s \ell) R_b T_g \exp-(\beta - \sigma_s)x] dx / 4k_s \sigma_s (1 - R_b R_g \exp(-2\sigma_s \ell)) \end{aligned}$$

Therefore, the total transmitted heat flux at the sample gas boundary arising from the light absorbed between x and $x + dx$ is

$$\frac{I_0 \beta T_g [\exp-(\beta + \sigma_s)x] + R_b \exp(-2\sigma_s \ell) \exp[-(\beta - \sigma_s)x]}{k_s \sigma_s (1 - R_b R_g \exp(-2\sigma_s \ell))} dx$$

Integrating from 0 to ℓ , we obtain the amplitude of the total thermal disturbance transmitted to the gas:

$$\theta = \frac{I_0 \beta T_g}{4k_s \sigma_s (1 - R_b R_g \exp(-2\sigma_s \ell))} \frac{1}{\beta + \sigma_s} [(1 - \exp(-(\beta + \sigma_s)\ell)) + \frac{R_b}{\beta - \sigma_s} (\exp(-2\sigma_s \ell) - \exp[-(\beta + \sigma_s)\ell])] \quad (18)$$

A modest amount of algebraic manipulations will convert this expression into the expression obtained by Rosencwaig and Gersho (Eq. (13) above).

This approach, though admittedly less rigorous than the boundary value approach, is more physical in nature and has the advantage of producing a formula which better illustrates the wave nature of the photoacoustic response. In particular, the first term in the square brackets of Eq. (18) represents the contribution to the transmitted thermal wave from the thermal wave within the sample that initially travels towards the gas. The second term corresponds to the thermal wave in the sample that originally travels towards the backing; hence the factor R_b . All of the multiply reflected waves will interfere at the sample-gas boundary and this thermal wave interference will affect the photoacoustic response^(32, 33). The factor $(1 - R_b R_g \exp(-2\sigma_s \ell))^{-1}$ may be thought of as being related to the "Q of the cavity" or the "finesse of the etalon;" as $e^{-\sigma_s \ell}$ becomes small the interference effects will become less noticeable. If $e^{-\sigma_s \ell} \sim 0$, then the thermal waves reflected from the sample-backing boundary will not be able to reach the sample gas boundary before being damped to zero, and the thermal properties of the backing will no longer affect the photoacoustic signal. For thin samples (ie, $\ell \ll \lambda_s$), many more multiple reflections will occur before the thermal waves damp out. In this case, the interference effects will be more significant,

and we should expect to see this in an analysis of our very thin carbon samples. Note that the sign of R_b determines whether or not there will be a 180° phase shift in thermal waves reflecting from the sample-backing boundary^(32, 33); this will be an important consideration in analyzing our photoacoustic results.

The above thermodynamical argument of Rosencwaig and Gersho may again be used here to obtain the pressure fluctuations from the transmitted thermal wave. The result is the same:

$$\Delta P(t) = \frac{\gamma P |\theta| \cos(\omega t - \pi/4 + \phi)}{\sqrt{2 k_g a_g T}}$$

We now address ourselves to the question of the effect of the additionally absorbed radiation due to the reflectivity of the backing. As explained in the introduction, we have developed this photoacoustic system to detect elemental carbon which has been loaded onto filter substrates. Some widely used filter materials are teflon, quartz fiber, and cellulose ester. All of these filter media appear white indicating that they are diffuse reflectors exhibiting little or no absorption in the visible. In what follows, we shall call the reflectivity R_f of a filter the fraction of incident light that is diffusely scattered backwards from the filter substrate. This reflectivity is about 50% for the Teflon filters used in this study and is about 90% for Millipore filters.

This backward scattered radiation passes back through the sample causing additional absorption and hence additional photoacoustic signal. We shall compute this additional response using the method of multiple reflections of thermal waves. This effect could just as well be computed by solving the appropriate boundary value problem.

We again refer to Fig. 4. The heat flux generated by light absorbed between x and $x + dx$ is now

$$\frac{1}{2}\beta I_0 R_f \exp(-\beta l) \exp[-\beta(l - x)]dx = \frac{1}{2}\beta I_0 R_f \exp(-2\beta l) \exp(\beta x) dx.$$

This initiates thermal waves at x with amplitude

$$\frac{\beta I_0 R_f \exp(-2\beta l) \exp(\beta x) dx}{4k_s \sigma_s}$$

The transmitted thermal wave at $x = 0$ due to the thermal wave within the sample that initially travels towards the gas is

$$\frac{\beta I_0 R_f T_g \exp(-2\beta l) \exp[(\beta - \sigma_s)x]dx}{4k_s \sigma_s (1 - R_b R_g \exp(-2\sigma_s l))} \quad (19)$$

The transmitted thermal wave at zero due to the thermal wave within the sample that initially travels toward the backing is

$$\frac{\beta I_0 R_f T_g R_b \exp(-2\beta l) \exp(-2\sigma_s l) \exp[(\beta + \sigma_s)x]dx}{4k_s \sigma_s (1 - R_b R_g \exp(-2\sigma_s l))} \quad (20)$$

Adding Eqs. (19) and (20) we obtain the amplitude of the thermal wave transmitted to the gas from light reflected from the filter and absorbed between x and $x + dx$. Integrating this expression from $x = 0$ to $x = l$ gives the total amplitude of the thermal wave transmitted to the gas:

$$\frac{\beta T_g I_0 R_f e^{-\beta l}}{4k_s \sigma_s (1 - R_b R_g \exp(-2\sigma_s l))} \left\{ \frac{(\exp(-\sigma_s l) - \exp(-\beta l))}{\beta - \sigma_s} + R_b \frac{(\exp(-\sigma_s l) - \exp(-2\sigma_s l) \exp(-\beta l))}{\beta + \sigma_s} \right\} \quad (21)$$

Therefore the thermal wave transmitted to the gas due to the incident light and the light reflected from the filter has amplitude

$$\sigma = \frac{\beta T_g I_0}{4k_s \sigma_s (1 - R_b R_g \exp(-2\sigma_s l))} \left\{ \frac{1}{\beta + \sigma_s} (1 - \exp[-(\beta + \sigma_s)l]) \right\}$$

$$\begin{aligned}
 & + \frac{R_b}{\beta - \sigma_s} (\exp(-2\sigma_s \ell) - \exp[-(\beta + \sigma_s)\ell]) \\
 & + R_f e^{-\beta \ell} \frac{1}{\beta - \sigma_s} (\exp(-\sigma_s \ell) - \exp(-\beta \ell)) \\
 & + \frac{R_b}{\beta + \sigma_s} (\exp(-\sigma_s \ell) - \exp(-2\sigma_s \ell) \exp(-\beta \ell)) \} \quad (22)
 \end{aligned}$$

The resulting pressure variation in the cell is

$$\Delta P'(t) = \frac{\gamma P |\theta'|}{\sqrt{2} \ell_g A_g T_0} \cos(\omega t - \pi/4 + \phi')$$

where

$$\tan^{-1} \phi' = \frac{\text{Im} \theta'}{\text{Re} \theta'}$$

Let us suppose that $\beta \gg |\sigma_s|$ to the point that, for all ℓ of interest, $\exp(-2\sigma_s \ell) \approx 1$ (the sample is thermally thin). In this case, Eq. () becomes

$$\theta' = \frac{T_g I_0}{2k_s \sigma_s} \frac{1 + R_b}{1 - R_b R_g} [1 - e^{-\beta \ell} + R_f e^{-\beta \ell} (1 - e^{-\beta \ell})]$$

If $R_f = 0$ then the photoacoustic signal would be proportional to $1 - e^{-\beta \ell}$. On the other hand, if $R_f = 1$, then the photoacoustic signal would be proportional to $1 - e^{-2\beta \ell}$, which is what one would expect.

As a final consideration, we compute the photoacoustic response that one would observe if the light were incident on the filter substrate first (see Fig. 1 and make the light incident from the left). Assuming that the sample does not significantly backscatter (as is the case for pure carbon black), then this would eliminate the additional absorption due to the reflectivity of the filter. We include this since we have essentially derived it already. By Eq. (21), the thermal wave transmitted to the gas will have amplitude

$$\theta'' = \frac{I_0(1 - R_f)\beta T_g}{2k_s\sigma_s(1 - R_bR_g2^{-2\sigma_s l})} \left\{ \frac{1}{\beta - \sigma_s} (e^{-\sigma_s l} - e^{-\beta l}) + \frac{R_b}{\beta + \sigma_s} (e^{-\sigma_s l} - e^{-2\sigma_s l} e^{-\beta l}) \right\}.$$

The corresponding pressure variation will be

$$P''(t) = \frac{\gamma P_0 |\theta''|}{\sqrt{2} \ell_g A_g T_0} \cos(\omega t - \pi/4 + \phi'')$$

where

$$\tan^{-1} \phi'' = \frac{\text{Im} \theta''}{\text{Re} \theta''}$$

II. OPTICAL ATTENUATION

In this section we give an analysis of the method of carbon detection denoted as optical attenuation. The basis of this technique consists of measuring the amount by which a beam of light is attenuated after passing through a sample deposited on a filter substrate.

Most filter materials diffusely scatter any light which passes through them. However, the degree to which this light is scattered may vary depending upon the type of filter material used. For example, if one passes a laser beam through an unloaded teflon filter, a small diffraction pattern is observed on a screen placed behind the filter indicating that the filter medium consists of narrow striations instead of small holes. In order to eliminate effects such as these, a piece of opal glass may be placed directly behind the filter. This is the so-called integrating plate method⁽¹⁶⁾. Some filter substrates, such as cellulose esther, are very good scatterers, so that the additional opal glass is not needed in the detection system. This technique has been used extensively by another group⁽¹⁷⁾ for quite some time.

Another reason for wanting a scattering surface behind the filter is that small particles not only absorb, but they scatter as well. The opal glass or the filter substrate should, to a very good approximation "integrate out" or eliminate the effect of forward scattered radiation by the particles on the filter. Backscattered radiation, however, is still a problem. One investigation⁽¹⁹⁾ has found that the specular reflectivity of an optically thick layer of soot is about 2.5%. Hence we may safely neglect backscattered radiation for the case of pure

elemental carbon. However, ambient aerosols contain large quantities of scattering particles such as $(\text{NH}_4)_2\text{SO}_4$. The presence of these types of particles will lead to significant backscattered radiation as well as multiple scattering within the sample medium itself leading to increased absorption.

The experimental set up, then, is to have light of intensity I_0 incident on the sample side of a filter loaded with soot. The unloaded side of the filter is placed next to a piece of opal glass and a detector is placed immediately behind the opal glass (see Fig. 5). The first

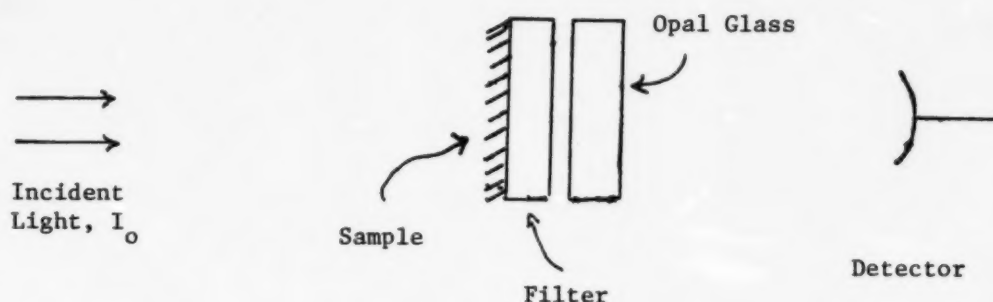


Fig. 5 Schematic of the Optical Attenuation System

step in the process is to measure the amount of light passed by a blank (unloaded) filter. The detector sees an intensity $I_0(1 - R_f')$ where R_f is defined above and where R_f' includes the effect of multiple scattering between the opal glass and the back side of the filter (see Eq. 24 below). We point out here that R_f' (or R_f) is different from filter to filter so that each filter used must be preanalyzed. The preanalyzed filter is then loaded with a sample of thickness ℓ . The intensity of the light passed by the loaded filter is then $I_0(1 - R_f')e^{-\beta\ell}$ where β is the absorption

coefficient of the sample in cm^{-1} . The amount of light backscattered by the filter (we neglect, by the above, the light backscattered by the soot) is $I_0 R_f e^{-2\beta l}$, and the amount of light absorbed by the sample is

$$I_0 (1 - e^{-\beta l}) + I_0 R_f e^{-\beta l} (1 - e^{-\beta l}).$$

We consider only the first term in the expression for the light absorbed by the sample and define the absorptance

$$A \equiv 1 - \frac{X_u}{X_L} = 1 - e^{-\beta l}, \text{ where} \quad (23)$$

X_u = fraction of light transmitted by an unloaded filter = $(1 - R_f)$

X_L = fraction of light transmitted by the loaded filter = $(1 - R_f) e^{-\beta l}$

$$\text{We may also compute } \beta l = -\ln(1 - A) \quad (24)$$

Some investigators have expressed concern over the fact that a different value of transmission (X_u/X_L) is observed depending upon whether the particles face the incident beam or are sandwiched between the filter and the opal glass. This effect is easy to understand and is included here for completeness. This section will also serve as a theoretical foundation for experiments to be discussed presently involving layers of scattering particles deposited on carbon loaded filters (see end of Section V).

Consider Fig. 6. If we assume that the filter and opal glass surfaces

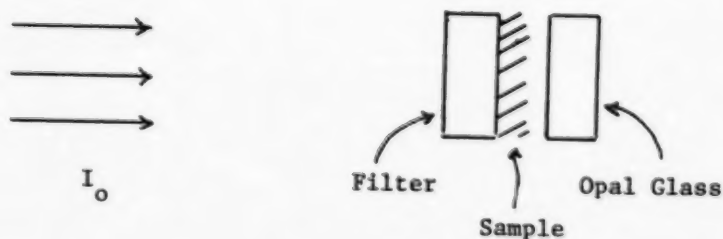


Fig. 6 Sample sandwiched between opal glass and filter.

act as parallel plane reflectors and ignore the phase of the incoming light, then the transmitted light due to multiple reflections between the filter and opal glass is

$$\begin{aligned}
 & I_0(1 - R_f) e^{-\beta l}(1 - R_g) + R_g e^{-\beta l} R_f e^{-\beta l}(1 - R_g) \\
 & + (R_g e^{-\beta l} R_f e^{-\beta l}) R_g e^{-\beta l} R_f e^{-\beta l}(1 - R_g) \\
 & + \dots + (R_g e^{-\beta l} R_f e^{-\beta l})^n(1 - R_g) + \dots \\
 & = I_0(1 - R_f)(1 - R_g)e^{-\beta l} + \frac{(1 - R_t)(1 - R_g)R_g R_f e^{-2\beta l}}{1 - R_f R_g e^{-2\beta l}} \\
 & = I_0 XL
 \end{aligned}$$

where R_g is the reflectivity of the opal glass and XL is defined above.

The light transmitted by the unloaded filter is

$$\begin{aligned}
 & I_0(1 - R_f)(1 - R_g) + \frac{(1 - R_f)(1 - R_g)R_f R_g}{1 - R_f R_g} \quad (24) \\
 & = I_0 X_u \text{ where } X_u = 1 - R'_f
 \end{aligned}$$

If we let $T = X_u/XL$, then

$$T = e^{-\beta l} + \frac{R_g R_f e^{-2\beta l}}{1 - R_g R_f e^{-2\beta l}} \quad 1 + \frac{R_g R_f}{1 - R_g R_f} \quad (25)$$

This is clearly not the way to measure absorption coefficients.

III. EXPERIMENTAL TECHNIQUES

The detector used in these experiments was designed so that simultaneous measurements of photoacoustic signal and optical attenuation could be made. The cylindrical cell was 1.3 cm in diameter and 0.3 cm long, and was equipped with a Knowles model 1759 electret microphone. The input window was glass and the output window was opal glass. The scattering side of the opal glass was adjacent to the back of the filter substrate. Since the absorption coefficient of soot exhibits very little structure across the visible spectrum, a tungsten filament (GE 1000 W. quartz iodine) lamp was used due to the high degree of stability and resetability exhibited by this type of source. The voltage across the lamp was controlled with an autotransformer and the current through the filament was measured with an ammeter. Light from the lamp was collected by a lens and passed through a 1 cm cell filled with water to filter out infrared radiation (a cell 5cm long would have been better). The light beam was modulated with a PAR model 192 chopper before entering the cell, and the light transmitted through the cell as measured by a PAR model HR8 lock-in amplifier, and the output of the photodiode was measured with a digital voltmeter.

In order to calibrate the detection system, it was necessary to prepare a set of loaded filters containing known amounts of carbon. The carbon generator consisted of a burner tip enclosed within a chamber which was continually flushed with a mixture of nitrogen and oxygen at a flow rate of 20 l/min. Our goal in setting up the generation system was to allow ourselves the capability, if possible, of producing elemental carbon without the presence of organic carbon impurities.

A mixture of approximately 1 part propane and 5 parts oxygen fueled the flame at the burner tip. The gas which flushed the chamber consisted of about 90% nitrogen and 10% oxygen. This produced an elongated flame where the soot producing portion of the flame was contained almost entirely within a blue envelope. Under these conditions the rate of carbon production could be accurately controlled by adjusting the propane flow.

The output of the carbon generator was sampled by a dichotomous sampler (Environmental Research Co.) which loaded the carbon onto teflon filters (Ghia Corp. 1μ) at a flow rate of 16.7 ℓ /min. A Mettler balance was used to obtain filter weights before and after loading to within $\pm 10\mu\text{g}$.

IV. RESULTS

In Fig. 7 we show a plot of Absorptance vs loading along with a plot of $\beta\lambda$ vs loading. The consistency of the data indicates that the fraction of organic carbon compounds, if present in our source particulate, is constant from sample to sample. Since we have produced carbon samples run under varying flame conditions which fall on the same line as those in Fig. 7, we conclude that the carbon samples presented here are essentially elemental carbon.

The infrared-filtered light from the tungsten filament source had a broad band intensity distribution which ranged from about 1.25μ to 0.4μ . However, the 1P39 photodiode used for the transmission measurements had a blue sensitive response, so that the light used for Fig. 7 was essentially blue. The slope of the $\beta\lambda$ vs loading curve gives a specific extinction of $5.39 \text{ (m}^2/\text{g)}$. This is up to a factor of two lower than other values⁽³⁵⁾ for specific extinction obtained by transmission measurements through cells containing suspended soot particles. However, $5.39 \text{ (m}^2/\text{g)}$ compares very well with specific extinction measurements of diesel soot on millipore filters made by Hansen et al.⁽¹⁴⁾ Hence, the presence of the filter may perturb a determination of the atmospheric extinction coefficient of suspended soot particles in the atmosphere. Therefore, we confine ourselves to the task of calibrating an ambient soot monitor, postponing for the present, any further discussions of ambient soot absorption.

In Fig. 8 we show a plot of photoacoustic response vs loading for the same set of filters used for Fig. 7. The data for this figure was obtained at a chopping frequency of 100 Hz. A comparison of Fig. 7 and Fig. 8 suggests that the photoacoustic data does not saturate as quickly as does the absorptance data and that there is more scatter in the

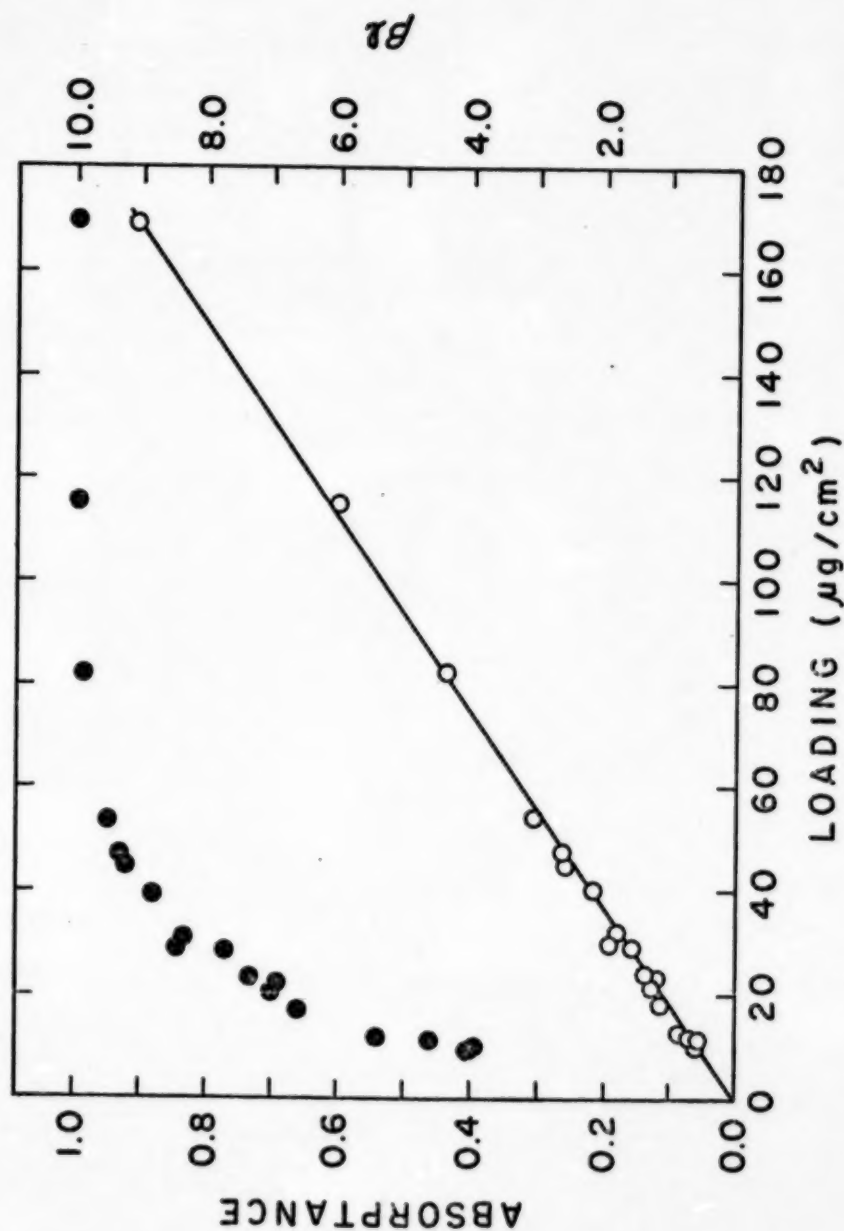


Figure 7. Plots of absorbance vs loading and optical thickness βl vs loading.

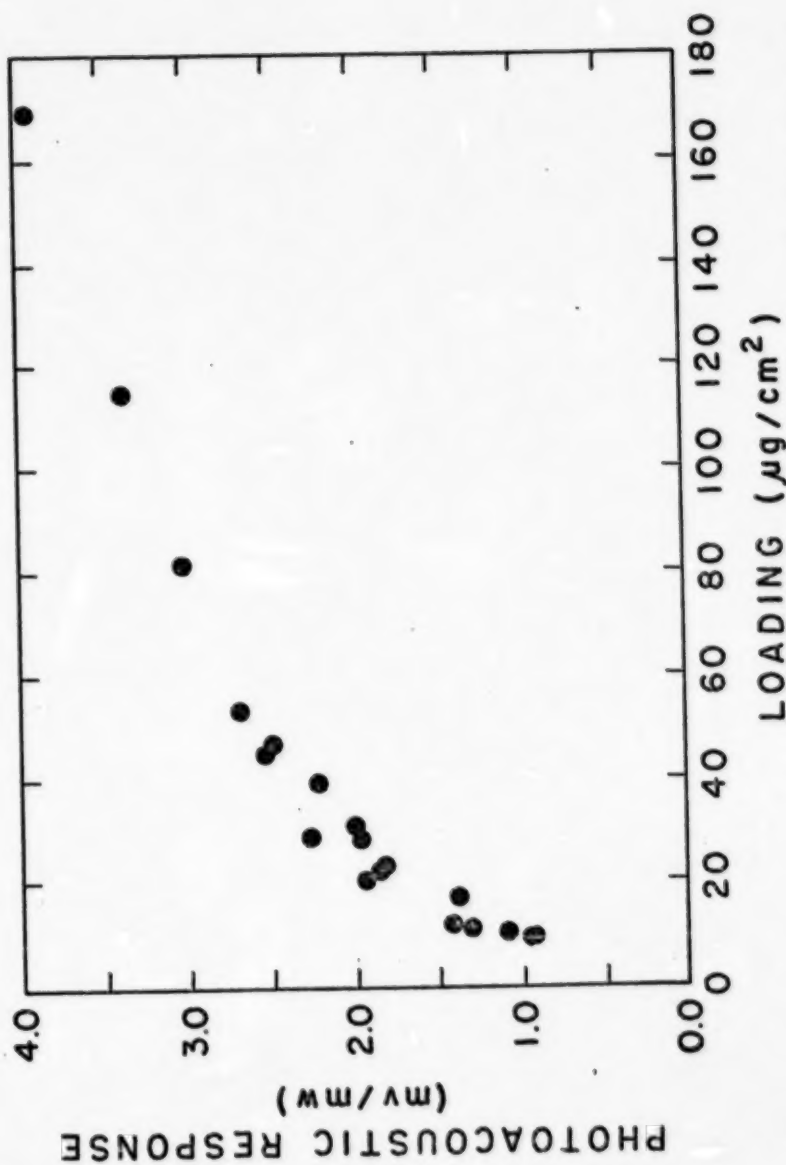


Figure 8. Plot of photoacoustic response vs loading for a 100 Hz chopping frequency.

photoacoustic data than there is in the absorptance data. We point out that if the same filter is repetitively inserted into the cell and sampled, the photoacoustic response for each reading agrees to within 3%. Hence the additional scatter in the low loading data points seems to be inherent. Two possible explanations for this additional scatter are (1) that the filter or backing substrates are not thermally thick so that each filter allows varying amounts of thermal energy to escape from behind, and (2) that the extra term derived in Section I accounting for the additional light absorbed by the sample due to reflection from the filter surface causes the scatter due to the variability of filter reflectivity. Note that, in our case, not only is the reflectivity of the filter important but we must also consider the reflection from the opal glass (as discussed in Section II above). Filters of high reflectivity would be affected less by the opal glass than filters of low reflectivity. We could also tacitly assume that filters of low reflectivity would be less thermally thick than filters of high reflectivity. The filters used in Fig. 8 had an average reflectivity R_f of 0.50 with values ranging from 0.45 to 0.53. A comparison of the reflectivity of each filter with the magnitude and sign of its corresponding scatter failed to show any conclusive correlation. Perhaps a photoacoustic cell without an opal glass output window would make the source of this scatter more apparent. We note, however, that if the filter substrates were not thermally thick, we could make them thermally thick by increasing the chopping frequency (see the part of Section I dealing with thermal waves). Hence, if this were the source of the scatter, then the scatter should disappear as chopping rate is increased. It will be shown below that this does indeed occur. We note, however, that an examination of Eq. 22 of Section I indicates

that this might also occur if the reflectivity of the filters were the source of the scatter. We also point out that both effects are consistent with the observation that the scatter is worse for the low loading points as seen in Fig. 8.

The fact that the photoacoustic signal at 100 Hz does not saturate is perhaps one of the most interesting features of this study. Consider Eq. 22 for the amplitude of the transmitted thermal wave, and let us suppose that $e^{-\beta l} \sim 0$. Suppose as well that $|\sigma_s|$ is small enough that $e^{-2\sigma_s l} \sim 1 - 2\sigma_s l$. In this case Eq. 22 becomes

$$\theta' \sim \frac{T_g I_0}{4k_s \sigma_s} \frac{1 + R_b - 2R_b \sigma_s l}{1 - R_b R_g + 2R_b R_g \sigma_s l}$$

It is evident from this expression that in order for the photoacoustic signal to increase after the sample has become opaque, as in Fig. 8, then R_b must be less than zero. Physically, this is easy to understand. If $R_b < 0$, then the thermal waves are interfering destructively at the sample gas boundary for a sample thickness l which is a small fraction of a thermal wavelength. As the sample thickness increases toward $\lambda_s/4$, the thermal waves build toward a constructive interference and the photoacoustic signal increases.

V. PRACTICAL CONSIDERATIONS FOR USING PHOTOACOUSTIC DETECTION AND OPTICAL ATTENUATION AS A MEANS OF DETECTING ATMOSPHERIC CARBON

We outline in this section a few of the considerations to be kept in mind if either of the techniques discussed in this report are to be used to establish quantitative levels of ambient carbon in the atmosphere. Whenever possible, the two techniques will be compared for their relative merits with regards to atmospheric carbon analysis.

We first recall, as stated earlier, that one of our primary concerns in preparing the carbon samples was to insure that the carbon generated was elemental in form. This was done by making sure that the soot-producing, cool region of the flame was almost completely enclosed by a blue, hot envelope so that any organic components produced in the cool region would be oxydized before escaping the flame. This may not be the way that ambient carbon is formed so that, in general, ambient carbon will have an organic and an inorganic component⁽¹⁴⁾. It is certainly widely accepted that the inorganic component is highly absorbing. However, the assumption that the organic component is non-absorbing may indeed be tacit. Consequently, if it were ones goal to construct a detector capable of detecting only ambient elemental carbon, then both of these methods would be perturbed by the presence of an absorbing organic component.

An obvious drawback to the 100 Hz photoacoustic data shown in Fig. 8 above is the occurence of scatter in the low loading points, especially since field loaded filters are likely to have low loadings of soot. Some possible sources of this scatter were outlined in the last section where it was noted that it would be responsible to expect that this scatter would disappear at higher chopping frequencies. To illustrate this effect, we first show, in Fig. 9, the photoacoustic data obtained

for a 10 Hz chopping frequency. The samples used for this plot are the same as those used for Fig. 8 except for the four points denoted by squares. These carbon samples were produced in a very cool, fuel-rich flame. A filter lightly loaded with this type of carbon has a reddish brown appearance indicating that the sample has a large blue absorbing organic carbon component. If a sample of this "red soot" is deposited on a quartz filter and heated to a temperature of about 400°C, the soot turns grey and there is an overall sample weight loss of about 20%.⁽³⁶⁾ It should be noted that all four of these organic carbon points in Fig. 9 are very heavily loaded and optically thick with $\beta L > 4$ for all four points. We also point out, as indicated earlier, that there is a large amount of scatter in the 10 Hz data; even more than is present in the 100 Hz data shown in Fig. 8.

Now consider Fig. 10 where a plot of photoacoustic response vs loading obtained with a 1000 Hz chopping frequency is shown for the same set of filters used for Fig. 9. When Fig. 10 is compared with Fig. 9 the following facts are immediately obvious: the scatter has all but disappeared from the 1000 Hz data, and the organic carbon points have shifted away from the inorganic carbon points in comparison with their relative positions in the 10 Hz data.

The reasons for the disappearance of the scatter for the high chopping frequency data have already been discussed. The very interesting fact that the relative photoacoustic response for the organic and inorganic carbon points changes with respect to chopping frequency is related, we believe, to the fact that photoacoustic spectra can be obtained on opaque samples⁽³¹⁾. Physically this is because only these thermal waves which are generated within one thermal wavelength of the sample gas boundary can

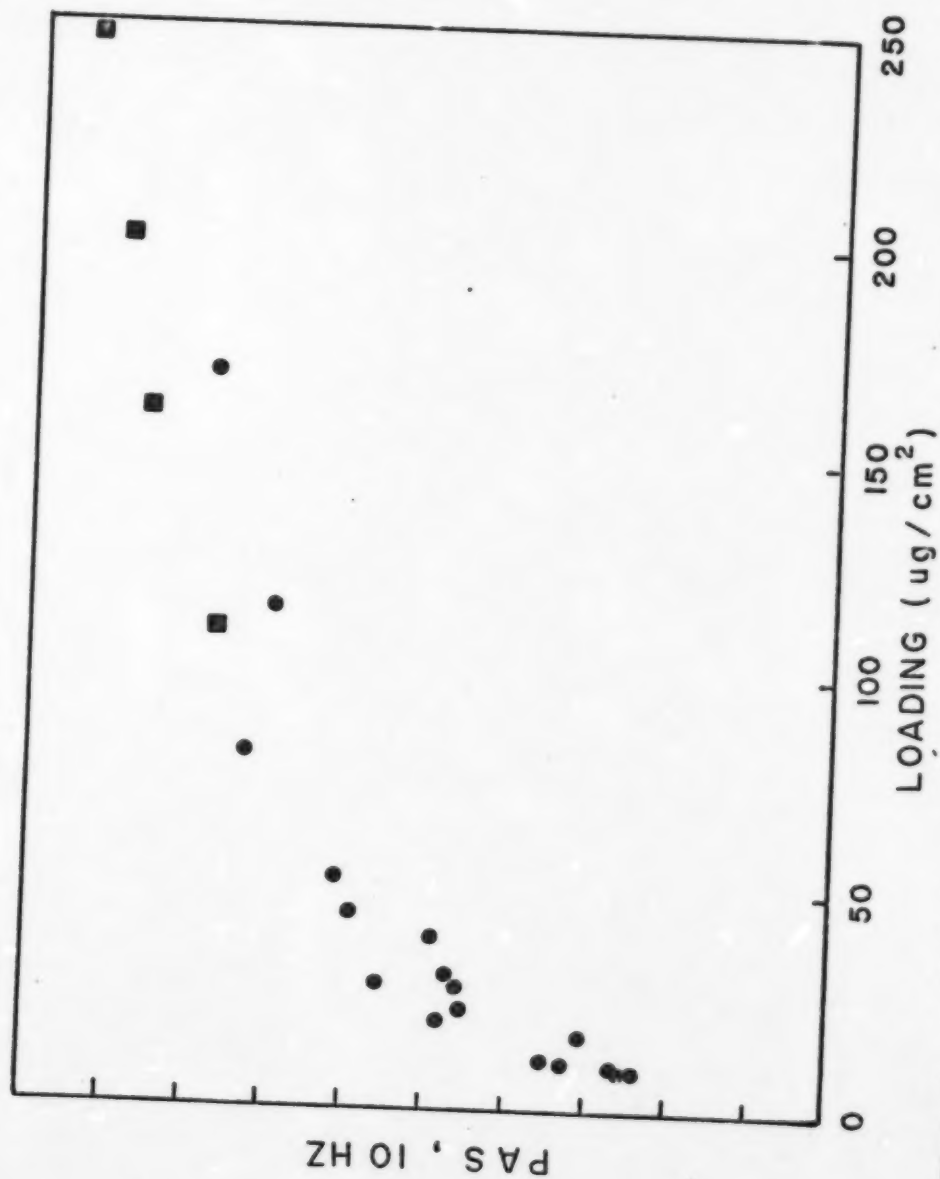


Figure 9. Plot of photoacoustic response vs loading for a 10 Hz chopping frequency. Samples containing organic carbon are denoted by squares.

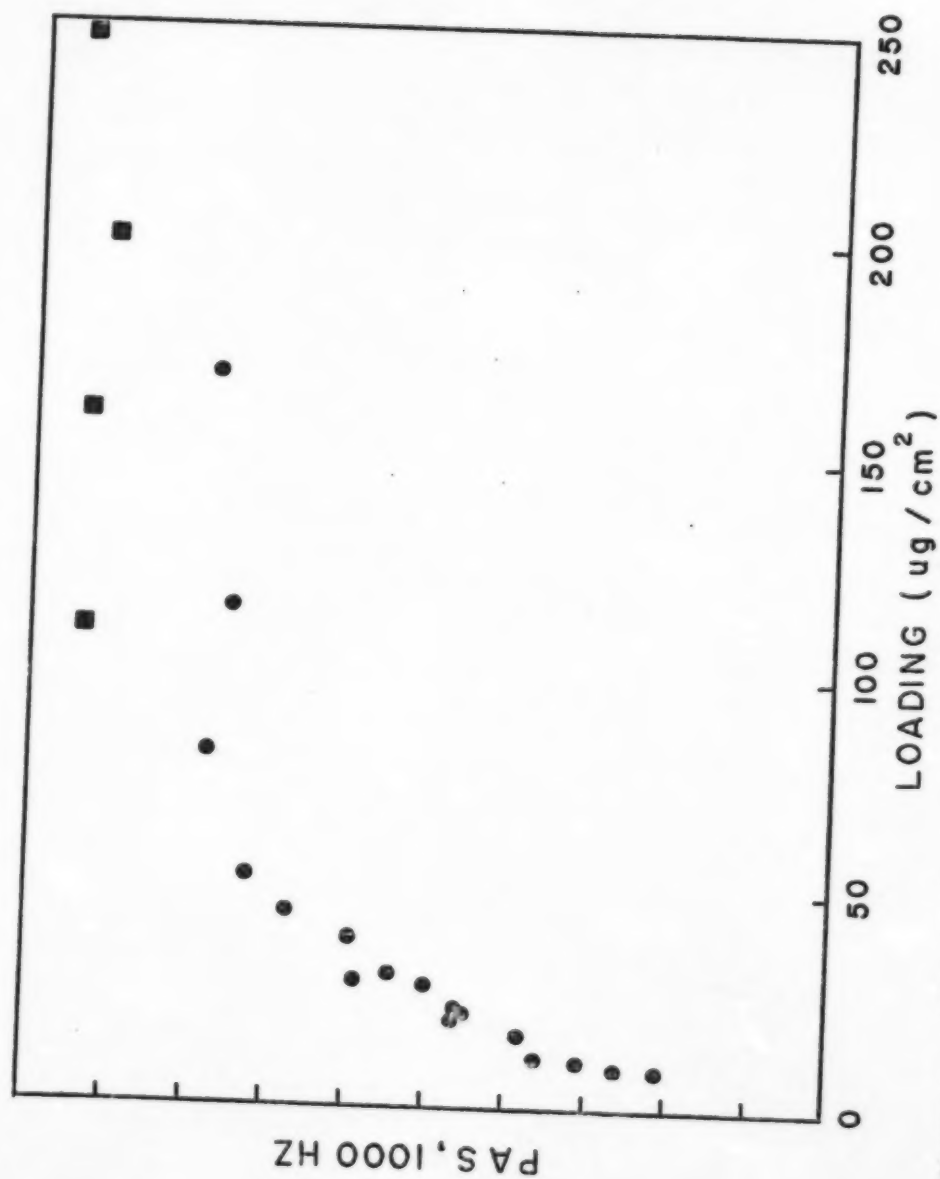


Figure 10. Plot of photoacoustic response vs loading for a 1000 Hz chopping frequency. Samples containing organic carbon are denoted by squares.

transmit themselves to the gas. If $A_s \gg \beta$, then it doesn't matter that the overall sample is optically thick; only a thin layer of sample adjacent to the gas responds photoacoustically to the absorbed light. We can see this from Eq. 22 for the amplitude of the transmitted thermal wave if we let $|\sigma_s| \ell \gg \beta \ell > 3$ to obtain

$$\theta' \sim \frac{T_g I_0}{4k_s \sigma_s^2} \beta.$$

The 1000 Hz case shown in Fig. 10 is not as extreme as this; we suggest only that the effect is starting to manifest itself. As we chop at higher and higher rates, we sample more and more from the surface of the carbon. We conclude then, for the particular organic carbon component that we have produced, that the organic component resides mainly on the surface of the inorganic component, and moreover, that the organic carbon component is more highly absorbing than the inorganic component. Note that if the organic component had been less absorbing than the inorganic component, then the organic points would have been shifted downwards. Since the imaginary part of the index of refraction of inorganic carbon is fairly constant⁽¹⁴⁾ one might be able to obtain useful information regarding the organic components of ambient carbon samples and hence infer their sources and potential health hazards by using high chopping frequencies and scanning the wavelength of the optical source.

As discussed in the introduction, a significant amount of scattering particulates is certain to be present in any ambient sample. Hence, it is important to understand how both methods of carbon analysis outlined here are affected by the presence of scattering particles. We give only a qualitative discussion of the effect here; a quantitative analysis

would be exceedingly difficult. The scattering properties of particulates depends on the size and shape of the particles and this is a complicated problem even for the relatively simple case of single scattering⁽³⁷⁾. Scattering particles loaded onto filter substrates might exhibit multiple scattering effects.

There are two effects which we shall concern ourselves with here:

(1) the backscatter of incident light away from the filter surface before any absorption takes place, and (2) multiple scattering within the sample leading to increased absorption.

If one visually examines a white filter loaded with soot and compares this to a white filter loaded with a mixture of $(\text{NH}_4)_2\text{SO}_4$ and soot, he will gain an intuitive notion as to the importance of backscattered light. The filter containing the scattering particles has a "milky" appearance compared to the filter loaded only with soot. Some authors have neglected the backscatter by claiming that the index of refraction of the scattering particles was very close to the index of refraction of their filter material; this is equivalent to saying that salt particles from a salt shaker would scatter light if placed on glass but would not scatter if placed on a large salt crystal. One group⁽³⁸⁾ has shown that filters of high reflectivity, such as Millipore, reduce the influence of backscattered light for the case of thin single scattering layers.

Multiple scattering will take place as the number of scattering particles increases. A criterion for single scattering used by Ref. 37 is that the total extinction due to scattering for suspended particulate should be less than 10%. Just how this relates to scattering particulates on a filter substrate is not certain; however we do point out that we have observed an extinction of greater than 10% for a $50 \mu\text{g}/\text{cm}^2$ sample

of pure $(\text{NH}_4)_2\text{SO}_4$ on a teflon filter. This extinction was ostensibly caused by backscatter due to the scattering properties of the filter material; hence the 10% criterion may not be valid here. We also mention the possibility of multiple scattering effects initiated by the fibrous nature of the filter medium itself. At any rate, multiple scattering within the sample will lead to increased absorption if absorbing particles are present.

Each of the methods of carbon analysis discussed in this report will be affected by the above phenomena. Both backscatter and multiple scattering lead to decreased transmission and thus to an increase in βL (see Fig. 6). However, backscatter tends to decrease the photoacoustic response while multiple scattering leads to increased absorption which increases the photoacoustic response; hence the two effects tend to cancel. It appears, then, that photoacoustic detection will give the better approximation to the true carbon mass in the presence of scattering particulates.

To illustrate these remarks, three teflon filters were loaded with different amounts of elemental carbon. After careful measurements of optical attenuation and photoacoustic response were made, about 200 μg of pure $(\text{NH}_4)_2\text{SO}_4$ was loaded on top of the carbon deposit. This should have produced a good backscattered component of light as well as multiple scattering best characterized by the remarks at the end of Section II (see Eq. (25)). The results of the optical attenuation measurements are summarized in Table 1. Here, L is the carbon mass before the $(\text{NH}_4)_2\text{SO}_4$ was loaded, βL is the extinction due to the carbon alone, $(\beta L)'$ is the extinction due to the carbon and $(\text{NH}_4)_2\text{SO}_4$; L' is the apparent carbon mass

$L(\mu g)$	βl	$(\beta l)'$	L'	$\frac{L' - L}{L} \times 100\%$
45	.305	.600	88	95%
90	.62	1.05	153	70%
149	1.02	1.53	223	49%

Table 1: Effects of a $(NH_4)_2SO_4$ layer on optical attenuation measurements.

after the addition of $(NH_4)_2SO_4$ using $(\beta l)'$ and the calibration curve in Fig. 6, and $((L' - L)/L) \times 100\%$ gives the percent overestimate of the carbon mass for optical attenuation due to the presence of the scattering particles.

To compare the perturbation of the photoacoustic response to the perturbation of optical attenuation due to the presence of the scattering layer, we will compute A and A' using βl and $\beta l'$ (see Eq. (22)) and compare this to R and R' where R is the photoacoustic response of the carbon alone and R' is the photoacoustic response of carbon plus the scattering layer. The results of these measurements are given in Table 2. Notice that the

L	A	A'	$R(\frac{mO}{mW})$	$R'(\frac{mO}{mW})$	$\frac{A' - A}{A} \times 100\%$	$\frac{R' - R}{R} \times 100\%$
45	.263	.451	.49	.61	71%	25%
90	.462	.650	1.0	1.05	41%	5%
149	.639	.783	1.35	1.35	23%	0%

Table 2: A comparison of the effect of a scattering layer upon measurements of absorptance A and photoacoustic response R for three loading values.

percent perturbation diminishes for both techniques as the carbon mass loading increases as one would expect. Notice also that, in each case, the perturbation to the absorptance measurements exceeds the perturbation to the photoacoustic measurements. Indeed, the effect has all but disappeared photoacoustically for the 90 μg and 149 μg samples. We accept these results with reservation, noting that only three filters were analyzed and that this is not the way scattering particles are distributed among absorbing particles in ambient samples. We chose this method of investigation since the effects are theoretically understandable (see last part of Section II) and since the experimental difficulties were minimized. This lab is currently involved in preparing samples of carbon and $(\text{NH}_4)_2\text{SO}_4$ in known ratios and size distributions in order to better characterize the relative perturbation to each technique that the presence of scattering particles will produce.

Finally we mention the possibility that a significant quantity of $(\text{NH}_4)_2\text{SO}_4$ present in the sample may alter the thermal properties of the sample and thus perturb the photoacoustic response. We postpone any further discussion of this until adequately prepared mixed samples of $(\text{NH}_4)_2\text{SO}_4$ and inorganic carbon are available.

CONCLUSIONS

Photoacoustic detection appears to be a powerful technique for ambient carbon monitoring. The thermal wave mechanism underlying the production of the acoustic signal introduces additional structure over the relatively straightforward optical transmission method. Although at first glimpse this additional structure may appear to be a complication, it may well turn out that the information provided by this structure will prove to be very useful. It appears that the photoacoustic technique is much less perturbed by the presence of scattering particles than is the method of optical attenuation; however, the effect is significant for both methods in the range of loadings expected for ambient samples. At any rate, the photoacoustic technique seems to provide the best approximation to the true carbon mass present in ambient samples of the two methods outlined in this report; indeed, the chief advantage of the optical attenuation method appears to lie in the simplicity and economy of the method. Ultimately, the effect of scattering particles must be theoretically and experimentally quantified in order that accurate carbon levels may be deduced.

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